

NATIONAL BUREAU OF STANDARDS REPORT

9043

SIXTH PRELIMINARY REPORT ON A SURVEY OF THERMODYNAMIC PROPERTIES OF THE COMPOUNDS OF THE ELEMENTS CHNOPS

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to

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1 February 1966



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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SIXTH PRELIMINARY REPORT ON A SURVEY OF THERMODYNAMIC PROPERTIES OF THE COMPOUNDS OF THE ELEMENTS CHNOPS

George T. Furukawa, Mary K. Buresh, Martin L. Reilly,
and George T. Armstrong

Heat Division, Institute for Basic Standards

Progress Report for the Period 1 October to 31 December 1965

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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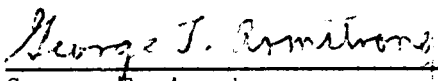
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FOREWORD

A study at the National Bureau of Standards (NBS), of which this is the sixth progress report, has been undertaken to meet the need of the National Aeronautics and Space Administration (NASA) for thermodynamic information on biologically related materials important to the space program for several reasons. Among these reasons are the necessity of inferring the maximum amount of useful chemistry of incompletely accessible environments, for which only limited information is available, the possibility of the occurrence of organic compounds naturally synthesized under primitive conditions, and the possibility of theoretically recovering part of the prebiological history of the earth.

This program is being carried out under the technical supervision of Dr. George Jacobs of NASA, and with the consultation of Dr. Harold Morowitz of the Yale University, Department of Molecular Biology and Biophysics, and Dr. C. W. Beckett of the Heat Division, Institute for Basic Standards (NBS). The contract (Contract No. R-138) was initiated 1 May 1964 and extended 29 April 1965. The program was extended by Amendment 1 for an additional year, beginning 1 July 1965. This report covers the second quarter of the extended contract.


George T. Armstrong
Supervisory Chemist
Project Leader

1. Review of Activity During the Reporting Period

1.1 Survey and Analysis of Low-Temperature Heat-Capacity Data

G. T. Furukawa, Mary K. Buresh, and M. L. Reilly

The low-temperature heat-capacity data on some polyhydroxy compounds related to sugars were examined, specifically sucrose, glucose, maltose, mannitol, lactose, galactose, and sorbose. Unfortunately, the lower temperature limit of these data is about 60°K. A large uncertainty is expected in any extrapolation to 0°K. The data on glycerol, which go down as far as 5°K, are being examined as a possible means for guide in the extrapolation.

In addition, the data on orthophosphoric acid, orthophosphoric acid hemi-hydrate, urea, furan, *l*-methionine, and *l*-serine were analyzed. Further work is in progress. Tables of thermodynamic properties on these substances are expected to be ready during the next quarter.

Survey of heat-capacity data on water, carbon dioxide, and ammonia was continued. Approximately 100 additional papers were examined.

A survey of the vapor-pressure data on the amino acids was made. A preliminary summary is given elsewhere in this report.

1.2 Surveys of Heats and Free Energies of Formation

G. T. Armstrong and M. N. Inscoe

During the reporting period covered by the present report the literature search for data on the ubiquitous biological compounds was continued. As a result of the literature survey thus far this file now contains 521 papers dealing with heats of reaction and equilibrium processes. This does not include materials referring to inorganic compounds.

Relatively few studies are made of heats of vaporization which are generally needed to calculate the thermodynamic properties of the vapors when only the data for the condensed phase have been determined. On the other hand, vapor pressure data are commonly reported and can be used to calculate the thermodynamic changes on evaporation. Attached to this report (Section 2) are critical reviews of the vapor pressures of two extremely important compounds in the field of exobiology, methane and ammonia. These reviews cover the vapor pressures from the critical point down to the lowest reported vapor pressures for each substance. In addition, in section 3 is presented a review of the vapor pressures of amino acids. This review reveals a great lack of information about the vaporization of the amino acids. In addition, the material contained in these reviews, a substantial body of critically evaluated thermodynamic and vapor pressure data on alcohols was received, which represents the work of the thermodynamics group at the Texas A and M University. A decision as to the best way this material can be made use of in this project is still under consideration.

2.1 Vapor Pressure of Methane

George T. Armstrong

In table 1 are found selected values for the vapor pressure of methane from 51°K to the critical point 190.6°K. These values are obtained from a critical review of the literature prior to 1955 [1]. A brief review of the sources is given below. A complete and detailed review of the data is given in Reference 1. The values found in table 1 were calculated using equation (1) for the solid, equation (2) for the liquid range below the normal boiling point, and equation (3) for the liquid above the normal boiling point.

$$\text{Log}_{10} P(\text{Torr}) = 7.69540 - 532.20/(T + 1.842) \quad (1)$$

$$\text{Log}_{10} P(\text{Torr}) = 6.61184 - 389.93/(T - 7.16) \quad (2)$$

$$\begin{aligned} \text{Log}_{10} P(\text{Torr}) = & 10.68631 - 595.546/T - 0.0348066T \\ & + 0.00013338T^2 - 1.7869 \times 10^{-7} T^3 \end{aligned} \quad (3)$$

The vapor pressure of solid methane has been measured by Hunter [2], Henning and Stock [3], Karwat [4], Freeth and Verschoyle [5], Tichner and Lossing [6] and Brickwedde and Scott [1].

The triple point is a fixed point through which both the vapor pressure functions for the vapor and the liquid pass. Independent determinations of the triple point were made by Olszewski [7], Hunter [2], Crommelin [6], Henning and Stock [3], Eucken and Karwat [9], Clusius [10], Wiebe and Brevoort [11], Freeth and Verschoyle [5], Fischer and Klemm [12], Kruis, Popp, and Clusius [13], Clusius, Popp, and Frank [14], Frank and Clusius [15], Brickwedde and Scott [1], Clusius and Wiegand [16], and by Staveley and Gupta [17]. The value obtained by Brickwedde and Scott for the triple point temperature was selected as the best value and a value of 87.50 Torr for the triple point pressure was selected as representative of the accurate determinations reported between 1931 and 1949.

The vapor pressure of liquid methane has been measured by Brickwedde and Scott [1], Tichner and Lossing [6], Henning and Stock [3], Cragoe [18], Wroblewski [19], Freeth and Verschoyle [5], Karwat [4], Eucken and Berger [20], Cardoso [21], Volova [22], Clusius [16], Clusius and Wiegand [22], Keyes, Taylor, and Smith [23], and by Bloomer and Parent [24].

The normal boiling temperature as a particular point on the vapor pressure function of the liquid was measured by Olszewski [7], Hunter [2], Henning and Stock [3], Keyes, Taylor and Smith [23], Cragoe [18], and by Brickwedde and Scott [1]. The selected value is 111.67°K, obtained by rounding the value of Brickwedde and Scott.

The critical point as a particular point on the vapor pressure function of the liquid was measured by Dewar [25], Wroblewski [19], Olszewski [7], Cardozo [21], Keyes, Taylor, and Smith [23], Bennewitz and Andreev [26], and by Bloomer and Parent [24]. Approximate average values of recent determinations of the critical temperature and pressure were selected as the best values.

Equations (1) and (2) pass through the selected temperature and pressure of the critical point, and equations (2) and (3) give the same temperature for the normal boiling point.

Table 1

Vapor Pressure of Methane

T °K	P(Torr) ^a	T °K	P(Torr)
Solid		Liquid	
51	0.0042	95	148.85
55	.0215	100	258.12
60	.1229	105	423.12
65	.541	110	661.01
70	1.939	111.67	760.00 (T _b)
75	5.88	115	993.28
80	15.58	120	1440.6
85	36.90	125	2023.9
90	79.55	130	2766.1
Triple Point		135	3691.3
90.66	87.50 (T _t)	140	4824.0
		145	6190.1
		150	7816.0
		155	9729.5
		160	11959
		165	14535
		170	17489
		175	20851
		180	24656
		185	28937
		190	33728
		190.6	34656 (T _c)

^a A Torr is 1/760 atm.

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2.2 Vapor Pressure of Ammonia

George T. Armstrong

In table 2 are found selected values for the vapor pressure of ammonia from 173°K to the critical point 405.6°K. These values are obtained from a critical review of the literature prior to 1953 [1]. A brief review of the sources is given below. A complete and detailed review of the data is given in Reference [1]. The values found in table 2 were calculated using equation (1) for the solid, and equation (2) for the liquid range below 250°K. Above 250°K, no analytical expression is given in Reference [1]; the selected values in that region are taken from a smooth curve drawn through the various reported data points.

$$\text{Log}_{10} P(\text{Torr}) = 9.98379 - 1627.22/T \quad (1)$$

$$\text{Log}_{10} P(\text{Torr}) = 9.95028 - 1473.17/T - 0.0038603T \quad (2)$$

The vapor pressure equation for solid ammonia was derived from data of Karwat [2], Postma [3], McKelvey and Taylor [4]. The mean absolute deviation of the pressures of the experimental points from the equation is about 0.75 percent.

The triple point is an invariant point on the phase diagram, and so the pressure and temperature can be selected separately from the available data. The value of -77.70°C (195.46°K) reported by Cragoe, Meyers, and Taylor [6] was selected as the best value for the triple point temperature. For the triple point pressure the value of 45.58 torr reported by Overstreet and Giauque [5] was selected. Many other measurements of the triple point temperature and/or pressure have been reported and are listed in Reference [1].

The equation for the vapor pressure of the liquid below 250°K (eq. (2)) is based upon experimental determinations reported by Postma [3], Bergstrom [7], Holst [8], Cragoe, Meyers, and Taylor [6], Overstreet and Giauque [5], Smits and Postma [9], Taylor and Jungers [10], McKelvey and Taylor [4], and by Henning and Stock [11]. The mean absolute deviation from equation (2) of all the vapor pressures reported from these sources is 0.3 percent. The equation for the vapor pressure of the solid intersects the equation for the vapor pressure of the liquid at the selected triple point temperature and pressure.

Above 250°K the values listed in table 2 were selected from a smooth curve through the data of Keyes [12], Cragoe, Meyers, and Taylor [6], and of Beattie and Lawrence [13]. The data above 250°K are very concordant. The mean absolute deviation of the pressure is less than 0.03 percent.

The normal boiling point and the critical point as special points on the vapor pressure function have been reported by numerous observers whose reported values are listed in Reference [1]. The selected values listed here were obtained in Reference [1] by a process of averaging the listed values.

Numerous other studies have been reported of the vapor pressure of ammonia, in addition to those from which the selected values were taken. These reported prior to 1914 were considered to be of historical interest only because of less accurate measuring instruments or of less pure ammonia than were used in later studies.

Table 2

Vapor Pressure of Ammonia

T ^o K	P(Torr) ^a	T ^o K	P(Torr)
Solid		Liquid	
173	3.78	285	4912.5
175	4.85	290	5804.2
180	8.78	295	6815.1
185	15.42	300	7956.6
190	26.27	305	9238.7
195	43.57	310	10,668.5
Triple Point		315	12,261
195.46	45.58	320	14,028
Liquid		325	15,988
200	64.92	330	18,135
205	93.91	335	20,498
210	133.21	340	23,089
215	185.51	345	25,919
220	253.97	350	28,999
225	342.20	355	32,344
230	454.28	360	35,973
235	594.70	365	39,906
239.78	760.00 (T _b)	370	44,146
240	768.43	375	48,702
245	980.78	380	53,597
250	1237.5	385	58,871
255	1546.9	390	64,558
260	1914.8	395	70,697
265	2348.9	400	77,334
270	2857.1	405	84,513
275	3448.1	405.6	85,400
280	4130.0		

^a A Torr is 1/760 atm.

References to Vapor Pressure of Ammonia

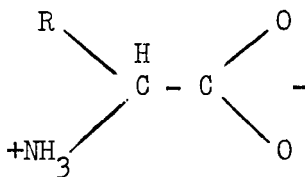
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3.1 Vaporization and Vapor Pressure of Amino Acids

George T. Furukawa

As a part of the literature survey of the vapor pressures of amino acids, the nature of the condensed phase or the crystal structure of the simplest of these substances was first investigated.

The amino acid molecule has in general an electric dipole or zwitter-ion configuration with the positive and negative charges separately centered about the nitrogen and oxygen atoms, respectively:



A polypole structure is assigned to the more complex amino acid molecules, e.g., cystine. In the crystalline state, the molecules (e.g., glycine, $\text{CH}_2\text{NH}_2\text{COOH}$) are held together by these electrostatic forces and by hydrogen bonding between the adjacent nitrogen and oxygen atoms [1]. Glycine, the simplest amino acid, exhibits a double molecular layer structure with relatively weaker van der Waals forces between the different double layers. The crystal can, therefore, be cleaved in the plane between the different double molecular layers. The nitrogen-oxygen distances within the single layer are 2.76 and 2.88 Å; while between the same double layer they are 2.93 and 3.05 Å [1], indicating that the inter-molecular forces between the two layers are different from those within the same layer.

The crystal structure of the next simplest amino acid, *dl*-alanine ($\text{CH}_3\text{CHNH}_2\text{COOH}$), is much more complex than that of glycine. Crystals of *dl*-alanine cannot be cleaved in any direction, indicating the alanine molecules to be bound tightly in a three-dimensional network. X-ray examination [2] has shown this to be indeed so with the molecules bound in a chain by electrostatic forces and hydrogen bonds between the nitrogen and oxygen atoms at 2.78 Å distance. The molecular chains are in turn bound to adjacent chains in a three-dimensional configuration by hydrogen bonds between the nitrogen and oxygen atoms of adjacent molecules at 2.84 and 2.88 Å distances. The crystal structure of *d*- or *l*-alanine may be different from that of *dl*-alanine just described.

The investigations of Bernal [3] on a number of amino acid crystals reported occurrences of polymorphism depending upon the relative positions of the molecular chains. These observations together with the detailed x-ray diffraction analyses on glycine and *dl*-alanine described above suggest

related crystal structures but of greater complexity with polymorphism for the other amino acids. Any vaporization data should, therefore, be carefully correlated with crystal structure at the temperature of the vapor-pressure measurement.

The higher densities of the amino acids also suggest a more tightly bound structure than the hydrocarbons. The densities at around room temperature of amino acids are in the range 1.4 to 1.7 g/cm³, while those of solid aliphatic hydrocarbons are around 0.7 to 0.8 g/cm³ and of aromatic hydrocarbons around 0.9 to 1.0 or 1.1 g/cm³.

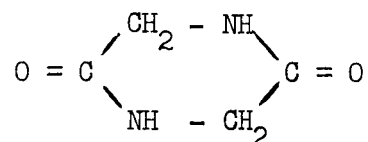
Because of the relatively low vapor-pressure of amino acids, vapor-pressure data on these substances are almost non-existent. The sublimation experiments of Gross and Grodsky [4] indicate that most of these substances can be vaporized without decomposition. Earlier Brown [5] found *l*-proline, *l*-leucine, iso-valine, *l*-phenylalanine, *d*-alanine, glycine, iso-leucine, glutamic acid, tryptophan, oxyproline, *l*-serine, and *l*-tyrosine to sublime, but not *d*-arginine, *d*-aspartic acid, or histidine. The following is a partial list of substances with which Gross and Grodsky conducted sublimation experiments.

Vaporization Data on Amino Acids and Related Substances
(From Gross and Grodsky [4])

<u>Substance</u>	<u>Vaporization Temperature</u> °C	<u>Temperature</u> <u>Range of Vaporization</u>	<u>Recovery</u> %
		°C	
<i>l</i> -alanine	138	193-200	98.5
<i>l</i> -ethionine	133	196-216	99.1
<i>l</i> -hydroxy proline	150	190-223	99.1
<i>l</i> -isoleucine	105	170-181	99.7
<i>l</i> -leucine	109	180-188	99.1
<i>l</i> -methionine	130	197-208	99.8
<i>l</i> -phenylalanine	130	176-184	98.2
<i>l</i> -proline	119	182-187	99.4
<i>l</i> -threonine	170	200-226	99.6
<i>l</i> -tryptophan	180	220-230	99.0
<i>l</i> -tyrosine	186	235-240	99.2
<i>l</i> -valine	102	178-188	99.5
<i>l</i> -aspartic acid		230-237	
<i>l</i> -cysteine	124	170-180	97.5
<i>l</i> -histidine		200	
<i>l</i> -lysine		160	
<i>l</i> -serine		160-170	
glycine	118	145-150	99.0
β -alanine	111	170-180	98.2

A vacuum of 0.3 mm Hg was used. The sublimation temperature was determined by raising the temperature at a rate of about one degree per minute and the sublimation was complete in about two to three hours in each experiment. The column designated "vaporization temperature" gives the initial temperature at which sublimation was evident and the column designated "temperature range of vaporization" gives the temperature where most of the material sublimed without apparent decomposition.

l-Histidine, *l*-serine, and *l*-aspartic acid gave low recovery, vaporized slowly, darkened extensively, and yielded glass-like sublimates. *l*-Lysine sublimate showed impurity phases. Gross and Grodsky [4] found *l*-arginine, *l*-asparagine, *l*-citrulline, *l*-cystine, *l*-diiodotyrosine, *l*-glutamic acid, *l*-glutamine, glutathione, and tartrine to decompose when subjected to the sublimation process. Earlier, Ostwald, Adams, and Tolbert [6] found glycine to form the diketopiperazine:



but not alanine. Gross and Grodsky [4] found no diketopiperazine formation with glycine or with any of the substances given in the above table.

Takagi, Chihara and Seki [7] investigated the vapor pressure of the α form of glycine crystal in the range 139 to 153°C using the Knudsen effusion method. The pressure ranged from 1.3 to 4.4 x 10⁻³ mm Hg. These values are considerably lower than the vapor pressure suggested for glycine (0.3 mm Hg at 118°C) in the sublimation experiments of Gross and Grodsky [4]. This may be due to possible differences in crystalline forms used. Takagi *et al.* calculated 31.18 ± 0.49 kcal/mole for the heat of sublimation of α -glycine from their vapor-pressure measurements. As to be expected this value is comparatively higher than the heats of vaporization of the hydrocarbons. Takagi *et al.* [7] suggest, on the basis of the value of their calculated heat of vaporization, the vaporization process to be from zwitter-ion in the crystal to molecular form in the gas. They consider zwitter-ion(c) to zwitter-ion(g) process to require about 103 kcal/mole.

In none of the vaporization experiments mentioned was the nature of the vapor species determined. Because of the zwitter-ion structure of the amino acid molecule, a dimer molecule in the vapor phase does not seem unlikely. Diketopiperazine found in the glycine sublimate by Ostwald *et al.* [6] is an extreme case of dimerization in which a condensation reaction occurred.

This preliminary literature survey has revealed a lack of accurate vaporization and vapor-pressure data on amino acids. The data that are available show that most of these substances can be sublimed without decomposition. Knudsen effusion and related methods (e.g., torsion method to check on vapor species) are suitable for vapor-pressure measurements. X-ray and mass spectroscopic examinations of the crystal and vapor phases, respectively, are essential in characterizing the system being investigated.

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